The Molecular Structure of Iodocarbonyl-π-cyclopentadienylpentafluoroethylrhodium

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RECENT studies[1,2] on the stereochemistry of conjugated olefinic ligands attached to transition-metal ions have indicated that the type of metal–carbon bonding is greatly influenced by the energy of the lowest antibonding molecular orbital on the ligand and that this is a sensitive function of the substituents around the conjugated system. Spectroscopic studies[3] on such perfluoroalkyl species as $CF_3Mn(CO)_5$ have suggested the possibility that even in saturated systems, substituents at the carbon atom may sufficiently lower the energy of the σ^* orbitals to enable them to participate in metal–carbon d–σ^* back donation.

Iodocarbonyl-π-cyclopentadienylpentafluoroethylrhodium, π-$C_5H_5Rh(CO)(C_2F_5)I$, is the first perfluoroalkyl transition metal to be crystallographically examined. The molecule, which has an asymmetric centre at the rhodium atom,[4] crystallizes as an ordered racemate in space group $P2_1/C$ with $a = 12{\cdot}41$, $b = 7{\cdot}82$, $c = 12{\cdot}63$ Å, $\beta = 109{\cdot}9°$, $Z = 4$. A three-dimensional X-ray structural analysis of the complex has been

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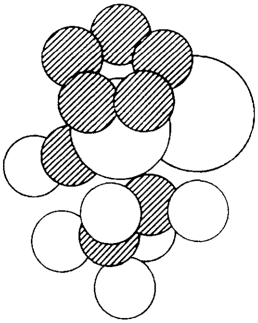
[1] M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, 1963, 365; 1964, 226; *Proc. Roy. Soc.*, 1964, *A*, **279**, 191.

[2] M. R. Churchill, Ph.D. Thesis, London, 1964.

[3] F. A. Cotton, *Inorg. Chem.*, 1964, **3**, 702, especially footnote 24a.

[4] J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 1964, 4200.

completed using conventional Patterson and Fourier techniques, and three cycles of full-matrix refinement of positional and anisotropic thermal parameters has converged the discrepancy index, R_1, to its present value of 7·84% for the 974 photographically-observed reflexions. The e.s.d.'s are ~0·03 Å for rhodium–light atom vectors, and ~0·05 Å for light atom vectors. The Figure shows the molecule (with carbon atoms shaded) projected on *b*. The formally d^6 Rh(+3) cation is in the expected octahedral environment (considering π-$C_5H_5^-$ as a formal tridentate ligand). The rhodium–carbon distances are 1·96 Å (carbonyl), 2·09 Å (perfluoroethyl), and 2·24 Å (mean of π-cyclopentadienyl carbon atoms). Having made the correction of 0·07 Å for the difference in covalent radii between *sp* and sp^3 hybridized carbon, the rhodium–carbonyl bond length is decreased by only 0·06 Å with respect to the rhodium–C_2F_5 bond. This is in marked contrast to the case of π-$C_5H_5Mo(CO)_3C_2H_5$, in which the molybdenum–carbonyl bond is 1·97 Å and the molybdenum–ethyl bond is 2·38 Å.[5] However, the markedly different stereochemistry of the molybdenum complex precludes any quantitative discussion of the metal–carbon distances. Any convincing evidence for double-bond character between the rhodium ion and the perfluoroethyl group in the present complex must be indirect, since variations in rhodium–carbon distances are not well documented. With any degree of double-bonding one would expect an increased C_α–C_β distance, and increased Rh–C_α–F and Rh–C_α–C_β bond angles as a result of the increased electrostatic repulsion between the Rh–C_2F_5 bond and the other bonds involving the α-carbon atom.[6] The observed carbon–carbon distance is 1·55 Å and all Rh–C_α–X angles are significantly greater than the ideal tetrahedral value of 109° 28′; Rh–C_α–C_β = 117·0°, Rh–C_α–F_1 = 110·5°, Rh–C_α–F_2 = 112·9°. This, coupled with the small difference in rhodium–carbon distance for the rhodium–carbonyl and rhodium–C_2F_5 bonds gives consistent evidence for some double-bond character in the rhodium–perfluoralkyl linkage, but further investigations are obviously necessary.



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[5] M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 1963, 273.
[6] R. J. Gillespie and R. S. Nyholm, *Quart. Rev.*, 1957, 339.